PATENT SPECIFICATION

DRAWINGS ATTACHED

1,104,294

Index at acceptance: —C2 C(1G1A1, 1G1D, 1G4A, 1G6A1, 3A13A3A1A, 3A13A3A1B, 3A13A3A1C, 3A13A3B1, 3A13A3B2, 3A13A3F2)

Int. Cl.: —C 07 c 17/10, C 07 c 29/12

COMPLETE SPECIFICATION

Production of Lower Alkanols and Lower Alkyl Bromides

I, RALPH WILLIAM KING, a British subject, of 19, Grosvenor Place, London, S.W.1., do hereby declare the invention, for which I pray that a patent may be granted to me and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to the production of alkyl bromides and alkanols from lower alkanes including cyclo-alkanes. The invention is primarily concerned with the production of methyl and ethyl alcohols from methane and ethane, and secondary normal C_3 to C_8 alcohols e.g., isopropanol, secondary normal butanol methyl n-propyl carbinol and di-ethyl carbinol from the corresponding normal paraffins.

The alcohols referred to are according to the prior art produced by a variety of methods. In the case of ethyl alcohol, isopropyl alcohol and secondary normal butanol, the most widely used method is by hydration of the corresponding olefin by the use of catalysts (e.g. sulphuric acid and alumina) at moderate to high pressures, and moderately elevated temperatures.

It is an object of the invention to provide an economic process for the production of lower alkanols starting from alkanes which are relatively low cost raw materials. All the paraffin hydrocarbons concerned are found widely in nature, i.e., in natural gas and petroleum deposits, and frequently employed as fuel. The olefins on the other hand are not found in nature in significant quantities and are manufactured by special cracking operations. Because of their greater chemical reactivity than the paraffins, they are much sought after as intermediates in the manufacture of many industrial chemicals and finished products in the fields of plastics, rubber, detergents and solvents. Ethylene in particular has assumed great importance in this connection over the past two decades, and is specially manufactured on a large industrial scale as an intermediate in the production of many products including ethanol. Ethane which is sometimes used as a feedstock in the manufacture of ethylene, and is also produced as a by-product when other feedstocks are employed, has little alternative value other than as fuel. Thus, the large price differential between ethylene and ethane provides a useful incentive for the manufacture of ethanol in particular starting from ethane as the raw material.

In other cases, such as the production of secondary normal pentanols, the corresponding paraffin (normal pentane) is sometimes employed as raw material, in a process which consists in chlorination of pentane to a mixture of amyl chlorides followed by alkaline hydrolysis of the amyl chlorides to the corresponding pentanol and sodium or other alkali metal chloride. This process involves a large usage both of chlorine and alkali — generally caustic soda—which it is a further object of the present invention to avoid.

The term "lower" as used herein to define alkanes, alkyl bromides or alkanols refers to such compounds having up to 8 carbon atoms in the molecule. Further, the alkanes, alkyl bromides and alkanols referred to herein include the cycloalkanes, cycloalkyl bromides and cycloalkanols.

Where reference is made in this specification to "alkyl bromide" this refers to the mono-bromide or mixture of mono-bromides, when such a mixture is formed.

According to the invention, a process for the production of a lower alkanol from the corresponding alkane comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the correspond-

[Pri

ing alkyl bromide and hydrogen bromide, separating the alkyl bromide and subjecting it to hydrolysis at an elevated temperature with water or steam as the hydrolysing agent
5 to produce the corresponding alkanol and hydrogen bromide, recovering the alkanol, oxidising hydrogen bromide recovered from the products of the bromination step and from the products of the hydrolysis step
10 to produce bromine and recycling the bromine thus produced to the bromination step.

The invention also includes a process for the production of a lower alkyl bromide from the corresponding alkane which comprises re-
15 acting an excess of the alkane with bromine at an elevated temperature to produce the alkyl bromide and hydrogen bromide, separating the hydrogen bromide from the alkyl bromide, recovering the alkyl bromide, oxidiz-
20 ing hydrogen bromide separated from the products of the bromination step to produce bromine and recycling the bromine to the bromination step.

The bromination reaction is preferably car-
25 ried out with the alkane and the bromine in the vapour state, preferably in the presence of a minor proportion of water vapour. However, it is possible to effect the bromination by contacting the alkane in vapour form with a solu-
30 tion of bromine in aqueous hydrogen bromide.

Broadly speaking, the bromination reaction may be carried out at a temperature of 80° to 450°C. and under a pressure of from 1
35 to 200 atmospheres absolute. When the bromine is in vapour form and no catalyst is employed, the temperature is preferably in the range 200 to 350°C., the pressure in the range 1 to 25, more preferably 5 to 15 atmos-
40 pheres absolute, and the contact time in the range 2 to 20 seconds depending on the particular alkane or mixture of alkanes employed. The temperatures and pressures preferred for the reaction are higher in the case of the
45 lower alkanes, methane and ethane, than in the case of the higher C_3 to C_8 alkanes.

It is also possible to effect the reaction at lower temperatures, i.e., in the range 125 to 180°C. with the use of catalysts, ultra-
50 violet light or a silent electric discharge, and in this case the bromine may be brought into contact with the alkane vapour as a solution in aqueous hydrogen bromide. A suitable catalyst for the bromination is tetraethyl lead
55 or other catalyst generating free radicals in the reaction.

In every case an excess of alkane should be maintained in the reaction zone, preferably such that the molar ratio of alkane to bromine
60 is in the range between 2:1 and 20:1, more preferably 3:1 and 10:1, suitably 5:1; this reduces the amount of dibromo and higher brominated products formed.

In the preferred method of procedure in
65 which bromine is introduced as vapour into

the bromination reactor, heat is evolved and a temperature rise occurs in the reactor, which temperature rise depends on the alkane used and the excess of alkane over bromine in the reactor feed.. Conditions are chosen so that 70 substantially complete reaction of the bromine takes place and only traces of unreacted bromine leave in the effluent from the reactor. Generally speaking, the reactor is operated adiabetically, though cooling arrange- 75 ments may be provided where the temperature rise would be so high as to cause appreciable decomposition of the alkyl bromides formed. Such decomposition which becomes significant at the upper end of the temperature 80 range leads to the production of olefins, which react in turn with bromine to form di-bromo alkanes; excessive temperatures should in consequence be avoided due to the larger amounts of by-products formed. The gaseous product 85 withdrawn from the bromination reactor consists mainly of alkane, alkyl bromide and hydrogen bromide and is treated as described below.

When the bromine is introduced into the 90 bromination reactor in solution, two effluent streams are withdrawn from the reactor, a liquid effluent consisting of aqueous hydrogen bromide poor in bromine, and a gaseous effluent consisting largely of alkane and alkyl 95 bromide which may contain smaller amounts of hydrogen bromide. The bulk of the hydrogen bromide formed during the reaction dissolves in the aqueous solution.

Whether bromine in the form of vapour or 100 in aqueous solution is used in the bromination reaction the gaseous effluent may be freed of hydrogen bromide by cooling and scrubbing with water or dilute aqueous hydrogen bromide to dissolve the hydrogen bromide 105 present in the effluent. Where there are traces of bromine present in the effluent, it may be scrubbed first with aqueous hydrogen bromide to remove the bromine, but this is not normally necessary. The scrubbing may be 110 carried out in scrubbers separate from the bromination reactor, or, when there are only small amounts of hydrogen bromide present in the gaseous product in the upper part of the bromination reactor. In the latter case 115 scrubbing liquid may be allowed to run down into the reactor proper to act as a temperature regulator.

The residual gaseous effluent after removal of hydrogen bromide may then be cooled, suit- 120 ably to a temperature in the range of 0° to 50°C. to condense all or part of the alkane, alkyl bromide, polybromoalkanes and residual water present in the gas. For C_4 to C_8 alkanes substantially all the alkane and alkyl bromide 125 is condensed by cooling to 50°C., but for the lightest alkanes, particularly methane and ethane, condensation is incomplete. The condensate may be separated into two liquid phases, an organic phase consisting of al- 130

kane, alkyl bromide and polybromoalkanes, and an aqueous phase. The liquid organic phase is fractionated to separate it into an alkane fraction, an alkyl bromide fraction and
5 a polybromoalkanes fraction. The alkane fraction .and any uncondensed alkane after removal' of impurities and preheating as necessary, are recycled to the bromination step.

Alternatively, particularly for C_1 to C_3 al-
10 kanes, the alkyl bromide may be separated from the gaseous effluent remaining after removal of hydrogen bromide, by scrubbing it with a suitable scrubbing liquid. It is convenient to use as the scrubbing liquid the
15 corresponding polybromo-alkanes formed as by-products during the reaction. On scrubbing the residual gaseous effluent with these compounds, the alkyl bromide and polybromo-alkanes present in the effluent are preferen-
20 tially dissolved. The undissolved alkane, after removal of impurities and preheating as necessary, is recycled to the bromination reaction zone. The solution of alkyl bromide in poly-bromo-alkanes is fractionated to separate the
25 alkyl bromide and the polybromo-alkanes are recycled for use as scrubbing liquor.

Any excess polybromo-alkanes not required for the process may be removed from the system and disposed of as such or sent to
30 a bromine recovery system, from which the recovered bromine may be returned to the process, preferably as an aqueous hydrogen bromide solution.

The alkyl bromide recovered from the bro-
35 mination reaction products may, according to the invention, be converted to the corresponding alkanol by hydrolysis. Water or steam may be used as the hydrolysing agent. The hydrolysis may be carried out in the vapour phase
40 using steam at high pressure, but, to avoid the need for vaporisation of large quantities of water, is preferably carried out in the liquid phase using water.

Liquid phase aqueous hydrolysis may be
45 carried out at a temperature in the range of 80° to 200°C., preferably 100° to 150°C., and a pressure sufficient to maintain a liquid phase in the reaction zone. The amount of water added to the hydrolysis reaction should
50 be sufficient to avoid high concentrations of hydrogen bromide being built up. Preferably the ratio by weight of water to hydrogen bromide exceeds 4 to 1 in the effluent from the hydrolyser. Higher concentrations of
55 hydrogen bromide slow down the rate of reaction and increase the corrosiveness of the hydrolysate.

Preferably some of the product alkanol removed in the effluent from the hydrolysis
60 reaction is recycled to that reaction together with any unreacted alkyl bromide. The recycle of alkanol has the advantage of increasing the solubility of bromide in the aqueous alcohol phase, thereby allowing the reaction to
65 proceed more rapidly. The unreacted alkyl

bromide and sufficient alkanol for recycle may be separated from the effluent from the hydrolysis reaction by a suitably controlled fractionation step.

Small quantities of the corresponding di-
70 alkyl ether are formed during the hydrolysis and these may be recovered as such from the withdrawn effluent, e.g. by fractionation, or recycled to the hydrolysis reaction where they may be converted to the alkanol.
75 The residual liquid effluent is fractionated to recover alkanol which may contain water as the only significant impurity.

Hydrogen bromide is recovered from both the bromination and the hydrolysis reactions.
80 That recovered from the bromination step is oxidised to produce bromine and, when hydrogen bromide is available from the hydrolysis step, it is oxidised together with the former.
85 The oxidation may be carried out either in the liquid phase or in the vapour phase, but is preferably carried out in the liquid phase to avoid the need for vaporisation of the hydrogen bromide solution in which form
90 the hydrogen bromide is normally obtained.

Liqiud phase oxidation of the hydrogen bromide may be controlled so that substantially all the bromine produced dissolves in the aqueous phase and does not form a
95 separate phase. The reaction is desirably carried out at a temperature from 15° to 200°C., preferably 50° to 130°C. and a pressure sufficient to maintain a liquid phase in the reaction zone.
100 The oxidation may suitably be carried out using either molecular oxygen or nitric acid. Molecular oxygen may be used alone or diluted with inert gases, e.g. in the form of air. A catalyst such as nitric oxide or nitric
105 acid, or a nitrate or nitrite or other nitrogen containing compound capable of liberating nitric oxide or nitrogen dioxide is preferably also present.

When nitric acid is employed as the oxidis-
110 ing agent for the reaction, the nitric acid is largely converted to nitric oxide and nitrosyl bromide in the course of the reaction. The nitrosyl bromide thus formed may be decomposed by contacting it with water or aqueous
115 hydrogen bromide to produce further nitric oxide. All or part of the nitric oxide may then be oxidised to nitric acid by contact with air and water as is well known in the art, and the nitric acid thus produced recycled to the
120 oxidation reaction.

Any organic impurities present in the solutions fed to the oxidation reaction zone are largely oxidised to carbon dioxide and water. The carbon dioxide and the other waste
125 gases may be vented, and the solution of bromine in aqueous hydrogen bromide collected and either passed directly to the bromination reaction or stripped of bromine and the bromine passed as vapour to the bromi-
130

nation reaction. In the latter case, the residual solution may be returned to the oxidation reaction or used as scrubbing liquor.

It will be appreciated that the invention provides a simple and convenient process for the conversion of a lower alkane to a corresponding alkanol employing only mildly exothermic reaction steps operating at moderate temperatures. The process is well-suited for continuous operation and, apart from alkane and oxygen, consumes only make-up quantities of bromine and catalysts.

Methods of procedure according to the invention are described below with reference to the accompanying drawings of which:

Figure 1 is a flow scheme of one method of carrying out the process of the invention, applied to the production of ethyl bromide or ethanol from ethane, and

Figure 2 is a flow scheme of another method of carrying out the invention applied to the production of n-amyl bromides of n-amyl alcohols from n-pentane.

Referring to Figure 1, fresh gaseous ethane feed is introduced under pressure into the system via line 1, recycle ethane leaving gas booster 100 is added via line 2, and the combined stream passes to the preheater 101 and thence via line 3 to the bromination reactor 102. Bromine vapour, together with some water vapour, is fed to the reactor 102 via line 4.

The hot gaseous product leaving the bromination reactor 102 via line 5 passes to the quench scrubber 103, where it is brought into contact with a dilute aqueous hydrogen bromide solution fed in via line 6. The gasliquid mixture leaving scrubber 103 passes via line 7 to the gas-liquid separator 104. Liquid consisting of a more concentrated solution of hydrogen bromide in water leaves the separator 104 via line 8 and passes to the oxidizer 113 referred to later.

Gas consisting mainly of ethane, bromoethanes and water vapour and substantially free from hydrogen bromide passes from the separator 104 via line 9 to the cooler-condenser 105. Liquid and uncondensed gas pass from cooler 105 by line 10 to the separator 106 where the mixture is separated into a gas stream leaving by line 11, a condensing bromo-ethane stream leaving by line 12, both of which pass to the absorber 107, and condensed water which leaves by line 13. The absorber 107 has a lower stripping section of smaller diameter than the main part of the column and equipped in the base with a reboiler (not shown), the function of which is to strip dissolved ethane from the liquid which leaves the base of the column by line 14 and passes to the fractionating column 108 where ethyl bromide is separated as overhead product from dibromoethanes and higher brominated products, which leave the base of the column 108 via line 15.

The greater part of the separated dibromoethanes and higher brominated products are cooled and then recirculated as scrubbing liquid to the top of the absorber 107 via line 16 whilst a smaller amount which approximately balances the production of these compounds in the bromination reactor 102 leaves the system via line 17. These compounds may either be worked up in a separate unit into saleable products, or passed to a different unit in which bromine is recovered in a convenient form for return to the process, i.e., as an aqueous solution of hydrogen bromide by line 33.

Ethyl bromide recovered as the overhead product from column 108 passes to the base of the hydrolysis reactor 109 via lines 18 and 19. Process water is routed to the hydrolyser 109 via lines 13 and 27, 20 and 19 being suitably preheated before entering the hydrolyser and any excess or deficiency of water is removed from or supplied to the system via line 21.

The hydrolyser 109 consists of a vertical tower equipped with internal baffles and an agitator in the lowest zone to secure intimate mixing of the separate liquid phases. Undissolved ethyl bromide remains substantially in the bottom zone of the hydrolyser, but ethyl bromide in solution in the aqueous-alcoholic phase passes into the middle and upper zones of the hydrolyser where its concentration is progressively reduced by chemical reaction with the solvent.

The liquid product from the hydrolyser is passed via line 22 to the fractionating column 110 in which unreacted ethyl bromide together with any diethyl ether formed and some of the ethanol is removed as overheads product and returned to the hydrolyser via line 23. The bottoms product from column 110 passes via line 24 to the fractionating column 111 from which the ethanol product consisting of at least 90% ethanol is removed by line 25 as overhead product. The bottoms product from column 111 consisting of an aqeous solution of hydrogen bromide, passes by line 26 to a further fractionating column 112, from which some of the water contained in the feed is removed by line 27 as overhead product and recycled to the hydrolyser 109. The bottoms product from column 112 leaves by line 28 which joins aqueous hydrogen bromide from line 8 and passes via line 29 to the stirred liquid phase oxidizer 113. This is supplied with oxygen via line 30 and nitric acid catalyst via line 31. Bromine make-up and recovered bromine from the bromine recovery unit are supplied to the oxidizer as an aqueous solution of hydrogen bromide by line 33.

A solution of bromine in aqueous hydrobromic acid from the oxidizer 113 passes via line 34 to the upper part of the stripping column 114 from the top of which bromine is

removed as a vapour together with some water vapour and passes via line 4 to the bromination reactor 102. A hot dilute aqueous hydrogen bromide solution leaves the base of column 114 and is passed to scrubber 103 via line 6.

The above description with reference to Figure 1, refers to the production of ethanol from ethane but the process and apparatus described may also advantageously be used for the production of methanol from methane.

Referring to Figure 2 which represents a scheme particularly suitable for the production of secondary normal amyl alcohols from normal pentane, the fresh hydrocarbon feed enters the process as a liquid from storage via line 1, is mixed with liquid recycle hydrocarbon from line 2 and passes to the vapourizer-preheater 101 which is equipped for steam or any other convenient form of heating. The preheated hydrocarbon vapour passes via line 3 to the reactor 102. Bromine vapour, together with some water vapour, is fed via line 4 to the bromination reactor 102.

In the reactor 102 substantially all the bromine reacts with the alkane to form a gaseous mixture containing unreacted alkane alkylbromide, hydrogen bromide and poly-bromo-alkanes. The hot gaseous product leaving the bromination reactor 102 via line 5 passes to the quench scrubber 103 where it is brought into contact with dilute solution of hydrogen bromide fed in via line 6. The gas-liquid mixture leaving scrubber 103 passes via line 7 to the gas-liquid separator 104. Liquid consisting of a more concentrated solution of hydrogen bromide in water leaves the separator 104 via line 8 en route to the oxidizer 113 (referred to hereinafter).

A vapour mixture of pentane, bromo-pentanes and water and substantially free from hydrogen bromide passes from the separator 104 via line 9 to the condenser 105. Condensed liquid from condenser 105 passes via line 10 to the separator 106 where it separates into a pentane-bromopentane phase which passes via line 11 to the fractionating column 107 and an aqueous phase which leaves via line 13 en route to the hydrolyser 109. The mixture entering column 107 is separated into an overhead stream consisting of unreacted pentane which leaves en route to the bromination reaction via line 2 and a bottoms product consisting of bromo-pentanes which passes via line 14 to the further fractionating column 108; here it is separated into an overhead product consisting of monobromo-pentanes which leaves via lines 18, 19 to the hydrolyser 109 and a bottoms product consisting of dibromopentanes and higher boiling materials which leaves by line 17 and passes to a separate bromine recovery unit.

Water from the separator 106 passes to the hydrolyser 109 via lines 13, 20 and 19 and any surplus or deficiency of water in the process is adjusted by bleeding water out of or into the process via line 21. A second aqueous phase containing some dissolved penta-nols and obtained from a later stage of the process passes into the hydrolyser by lines 27 and 20 and 19. Part of the aqueous streams fed to the hydrolyser is suitably preheated. Alcohol containing any unreacted bromopen-tanes from the hydrolyser is recycled to the hydrolyser via lines 35 and 19 from storage or from a separate pentanol purification unit.

The hydrolyser 109 consists of a vertical pressurised tower equipped with internal baffles and an agitator in the lowest zone to secure initimate mixing of the separate liquid phases. Undissolved bromopentanes remain substantially in the lowest zone of the hydrolyser, but bromopentanes in solution in the aqueous pentanol phase pass into the middle and upper zones of the hydrolyser where their concentration is progressively reduced by chemical reaction with the solvent.

The liquid leaving the hydrolyser passes via line 22 to the fractionating column 110 which is equipped with an overhead conden-sor 115 and a phase separator or dencanter 116. Overhead vapour leaving the column via line 23 and consisting of water, pentanol and unreacted bromopentanes is condensed and cooled in condenser 115, and the resulting condensate passes via line 24 to the separator 116 where the aqueous and sparingly soluble pentanol phases separate. The aqueous phase leaves via line 27, part being returned as reflux to the column 110 via line 26, the remainder being recycled to the hydrolyser 109. Crude pentanol product leaves the system via line 25 and may be used as such or further purified in another unit where it may be conveniently fractionated to give a bromo-pentane rich steam which is returned to the hydrolyser via line 35 and in which secondary normal pentanols are separated by distillation from primary normal pentanol which is formed in smaller quantities as a by-product.

The bottoms product from fractionator 110 consisting of a moderately concentrated solu-tion of hydrogen bromide in water leaves via line 28 and after joining the aqueous hydrogen bromide leaving separator 104 via line 8, passes to the oxidizer 113 via line 29.

Oxygen is continuously supplied to the oxi-dizer via line 30, nitric acid catalyst via line 31 and recovered and make-up bromine via line 33 as a solution of hydrobromic acid in water. Inert gas is continuously vented from the oxidizer via line 32. The oxidizer is provided with a stirrer. The oxidized product consisting of a solution of bromine in hydrobromic acid is continuously returned to the stripper 114 via line 34.

In the stripper 114 a gaseous overhead product comprising bromine with a little water vapour is removed and passed via line 4 to reactor 102. The residual liquid consisting of

hot dilute aqueous hydrogen bromide leaves the base of the stripper 114 via line 6 and is passed to the scrubber 103.

The system illustrated by Figure 2 may suitably be applied to the production of cyclo-alkyl bromides and cycloalkanols from the corresponding cycloalkanes having 5 to 8 carbon atoms, e.g. the production of cyclohexyl bromide and cyclohexanol from cyclohexane. An advantage of the process of the invention as compared with the oxidation process for the production of cyclohexanol is the absence of cyclohexanone from the product of the reaction. The invention is also applicable to alkyl-substituted cycloalkanes.

The fractionating columns shown in Figures 1 and 2 are provided as required with re-boilers, reflux condensers, pumps, vessels and other auxiliaries. The processes are fully continuous. Special corrosion resistant materials, for example titanium and its alloys, are employed as required by the corrosive nature of the process fluids.

The following Examples 1 and 2 illustrate the bromination and hydrolysis steps of the process of the invention. When combined with hydrogen bromide oxidation such as illustrated in Examples 3 and 4 they illustrate the whole process of the invention. In the Examples parts and percent means parts by weight and percent by weight respectively unless otherwise indicated.

EXAMPLE 1

Ethane and bromine in a molar ratio of 9:1 were reacted in the vapour phase in an elongated reactor. The reaction temperature was 303°C., the reaction pressure 1 atmosphere absolute and the contact time in the hot reaction zone 14 secs. The reactor product was analysed and found to be free of bromine. Of the organic brominated product 87.4% was ethyl bromide and 12.6% di-bromoethanes and higher brominated products. Thus, about 84% of the theoretical yield of ethyl bromide, based on bromine utilized, was obtained.

In another run ethane and bromine in a molar ratio of 3.2 to 1 were reacted in the vapour phase in a similar reactor. The reaction temperature was 319°C., the reaction pressure 1 atmosphere absolute and the contact time 39 secs. Again the reactor product contained no free bromine. 77.4% of the organic brominated product was ethyl bromide and 22.6% dibromo-ethanes and higher brominated products. Comparison of the two runs clearly indicates the importance of excess alkane in reducing the amount of poly-bromo-compounds produced.

1 part of ethyl bromide produced as described above was added to 9 parts of an ethanol-water mixture consisting of 40% ethanol and 60% water, and hydrolysed for 2 hours at 130°C. and 20 atmospheres pres-

sure. 93% of the ethyl bromide present was hydrolysed and the yield of ethyl alcohol, based on ethyl bromide hydrolysed, was over 97%.

EXAMPLE 2

A mixture of n-pentane (92% pure), and bromine vapour in a molar ratio of 4.7 to 1 was reacted in an elongated reactor the first part of which was maintained at a temperature of 265°C. The reaction pressure was one atmosphere absolute and the contact time in the hot reaction zone 12 secs. The effluent gases were passed through a scrubber maintained at 70°C. through which water was circulated, and then to a condenser in which the vapours were completely condensed. The bromine was quantitatively converted to hydrogen bromide and organic bromine compounds. 47% of the bromine introduced was found as hydrogen bromide dissolved in the scrubbing water.

The condensed phase was fractionated and analysed. 86% of the organic bromine compounds were found to monobromopentanes and 14% higher brominated products. The monobromopentanes were made up as follows:

1-bromo-n-pentane	13%
2-bromo-n-pentane	47%
3-bromo-n-pentane	31%
unidentified	9%

One part of the mono-bromo-pentanes obtained as above was hydrolysed with 15 parts of a 15% alcohol—85% water mixture for three hours at 145°C. 91% of the mono-bromo-pentanes was hydrolysed, with a yield of 92% of alcohols based on the bromo-pentanes hydrolysed.

The oxidation of hydrogen bromide using nitric acid as the oxidising agent recovered from the bromination and hydrolysis steps is illustrated in the following two Examples.

EXAMPLE 3

100 parts of an aqueous solution containing 20 parts of hydrogen bromide representing a typical product from the base of column 112 and separator 104 of Fig. 1 was refluxed for one hour with 5 parts of nitric acid. Evolution of nitric oxide gas which was rapid during the first 15 minutes became thereafter progressively slower and was negligible at the end of the period.

The liquid reaction product was distilled for 1½ hours to remove dissolved nitrosyl bromide, water lost by distillation being replenished every half hour. Bromine and water were collected in the distillate.

Analysis of the residue indicated that 89% of the original nitric acid and 82% of the original hydrogen bromide had reacted. The conversions corresponded closely to the reaction of one mole of nitric acid with three moles of hydrogen bromide.

Example 4

The experiment described above was repeated employing 100 parts of an aqueous solution containing 20 parts hydrogen bromide and 3 parts of nitric acid. The final analyses indicated that 94% of the original nitric acid and 53% of the original hydrogen bromide had reacted, again corresponding closely to the reaction of 1 mole of nitric acid with three moles of hydrogen bromide.

The bromine produced in each of Examples 3 and 4 was suitable for recycle for use in the bromination of additional quantities of alkane.

The bromination reactor 102 in Figures 1 and 2 may suitably consist of two consecutive reaction zones — an initial zone of diameter equal to at least half its length and designed to promote a high degree of mixing throughout the zone, and a final zone of smaller diameter but greater length than the initial zone in which back-mixing is minimised. The greater part of the reaction and consequent liberation of heat then takes place in the initial zone, thereby quickly preheating the incoming streams of bromine and alkane to a temperature at which the rate of reaction is rapid. The initial zone may be provided with a means for local heating, e.g. a suitably sheathed electric element, to initiate the reaction at plant start-up. The final zone is intended to achieve substantially complete conversion of bromine whilst avoiding the formation of excessive amounts of polybromoalkanes.

If required, an additional scrubber or other device, designed to eliminate mist caused by fine droplets of aqueous hydrogen bromide, may be provided in line 7 of Figure 1 or line 9 of Figure 2 to treat the gas leaving the first scrubber.

The process of this invention using an alkane and bromine as starting materials has two important advantages when compared with a process using chlorine in place of the bromine. Firstly, the alkyl bromides formed are more readily hydrolysed to the alcohol than are the corresponding alkyl chlorides, and satisfactory rates of hydrolysis of the bromides may be achieved in liquid phase hydrolysis at only moderately elevated pressures and at temperatures below 150°C. Secondly, hydrogen bromide is more readily and economically oxidised to bromine than hydrogen chloride is oxidised to chlorine, and hydrogen bromide may be oxidised easily in aqueous solution.

WHAT I CLAIM IS:—

1. A process for the production of a lower alkanol from the corresponding alkane, which comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the corresponding alkyl bromide and hydrogen bromide, separating the alkyl bromide and subjecting it to hydrolysis at an elevated temperature with water or steam as the hydrolysing agent to produce the corresponding alkanol and hydrogen bromide, recovering the alkanol, oxidising hydrogen bromide recovered from the products of the bromination step and from the products of the hydrolysis step to produce bromine and recycling the bromine thus produced to the bromination step.

2. A process for the production of a lower alkyl bromide from a corresponding alkane which comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the alkyl bromide and hydrogen bromide, separating the hydrogen bromide from the alkyl bromide, recovering the alkyl bromide, oxodizing hydrogen bromide separated to produce bromine and recycling the bromine to the bromination step.

3. A process as claimed in Claim 1 or 2, wherein the bromination reaction is carried out at a temperature of from 80° to 450°C. and a pressure of from 1 to 200 atmospheres absolute.

4. A process as claimed in Claim 3 wherein the bromination reaction is carried out with bromine in the vapour phase in the absence of a catalyst at a temperature from 200° to 350°C. and a pressure from 1 to 15 atmospheres absolute.

5. A process as claimed in Claim 3 wherein the bromination reaction is carried out using bromine in solution in aqueous hydrogen bromide in the presence of a free radical-generating catalyst or initiator at a temperature from 125° to 180°C. and a pressure sufficient to prevent appreciable evaporation of the aqueous hydrogen bromide.

6. A process as claimed in any of the preceding claims wherein the molar ratio of alkane to bromine in the bromination step is from 3 to 1 to 10 to 1.

7. A process as claimed in Claim 4 or Claim 4 and 6 wherein a gaseous stream containing unreacted alkane, alkyl bromide, polybromoalkanes and hydrogen bromide is withdrawn from the bromination step, is scrubbed with water or dilute aqueous hydrogen bromide to absorb the hydrogen bromide, and, after removal of water, alkyl bromide is separated from the residual gaseous effluent.

8. A process as claimed in Claim 7 wherein the residual gaseous effluent, after removal of water, is cooled and fractionated to separate an alkane fraction which is recycled to the bromination step, an alkyl bromide fraction and a polybromoalkanes fraction.

9. A process as claimed in Claim 7 wherein the residual gaseous effluent is scrubbed with liquid polybromoalkanes to absorb alkyl bromide and polybromoalkanes, the unabsorbed alkane is recycled to the bromination step, the scrubber liquid is fractionated to separate alkyl bromide from polybromoalkanes and the

polybromoalkanes are recycled to the scrubbing step.

10. A process as claimed in Claim 1 or in Claim 1 and any of Claims 3 to 9, wherein the hydrolysis of the alkyl bromide is carried out in the liquid phase at an elevated temperature using water as the hydrolysing agent, a liquid effluent comprising water, hydrogen bromide and alkanol is removed from the reaction zone, and the alkanol is recovered from this liquid effluent.

11. A process as claimed in Claim 10 wherein the hydrolysis is carried out at a temperature from 100° to 150°C. at a pressure sufficient to prevent appreciable evaporation of the liquid phase.

12. A process as claimed in Claim 10 or 11, wherein a part of the product alkanol removed from the hydrolysis zone is recycled to that zone to dissolve alkyl bromide.

13. A process as claimed in any of Claims 10 to 12, wherein the ratio by weight of water to hydrogen bromide in the hydrolysis zone is maintained above 4 to 1.

14. A process as claimed in any of Claims 10 to 13, wherein the liquid effluent removed from the hydrolysis zone is fractionated to separate an alkanol product fraction containing water as substantially the only impurity, an unreacted alkyl bromide fraction and an aqueous hydrogen bromide fraction.

15. A process as claimed in any of the preceding claims, wherein the hydrogen bromide oxidation is carried out in aqueous solution at an elevated temperature to form a solution of bromine in aqueous hydrogen bromide.

16. A process as claimed in Claim 15, wherein the oxidation is carried out at a temperature from 50° to 130°C. and a pressure sufficient to prevent appreciable evaporation of the aqueous solution.

17. A process as claimed in any of the preceding claims, wherein the hydrogen bromide is oxidised with molecular oxygen or nitric acid.

18. A process as claimed in Claim 17, wherein molecular oxygen is the oxidising agent and nitric oxide, nitric acid, or a nitrate or nitrite capable of yielding nitric oxide or nitrogen dioxide, is added as a catalyst.

19. A process as claimed in Claim 17, wherein nitric acid is the oxidising agent and nitric oxide formed during the oxidation and/or by decomposition of nitrosyl bromide formed during the oxidation, is oxidised to nitric acid which is recycled to the hydrogen bromide oxidation step.

20. A process as claimed in any of the preceding claims, wherein the starting alkane is methane and methyl bromide or methanol, as the case may be, is produced as product.

21. A process as claimed in any of Claims 1 to 19 wherein the starting alkane is ethane and ethyl bromide or ethanol, as the case may be, is produced as product.

22. A process as claimed in any of Claims 1 to 19, wherein the starting alkane is a normal paraffin with 3, 4 or 5 carbon atoms and the corresponding alkyl bromide or secondary normal alcohol, as the case may be, is produced as product.

23. A process as claimed in any of Claims 1 to 19, wherein the starting alkane is a cycloalkane or alkyl-substituted cycloalkane having at least 5 carbon atoms in the cycloalkane ring and the corresponding cycloalkyl bromide or cycloalkanol, as the case may be, is produced as product.

24. A process for the production of a lower alkyl bromide as claimed in claim 2 substantially as herein described.

25. A lower alkyl bromide when produced by a process claimed in Claim 2 or in Claim 2 and any of Claims 3 to 9 and 15 to 23 or in Claim 24.

26. A process for the production of a lower alkanol as claimed in claim 1 substantially as hereinbefore described.

27. A lower alkanol when produced by the process claimed in Claim 1 or in Claim 1 and any of Claims 3 to 23 or in Claim 26.

Fig. 1.

Fig. 2.

1104294

2 SHEETS
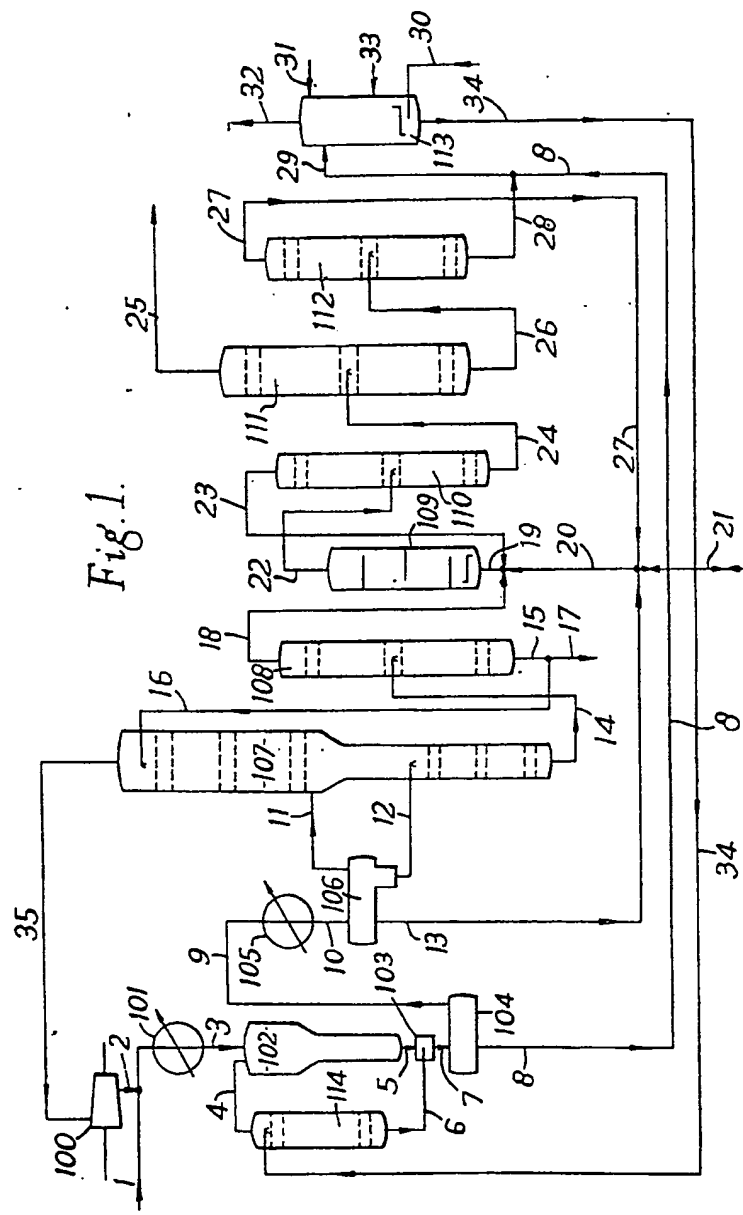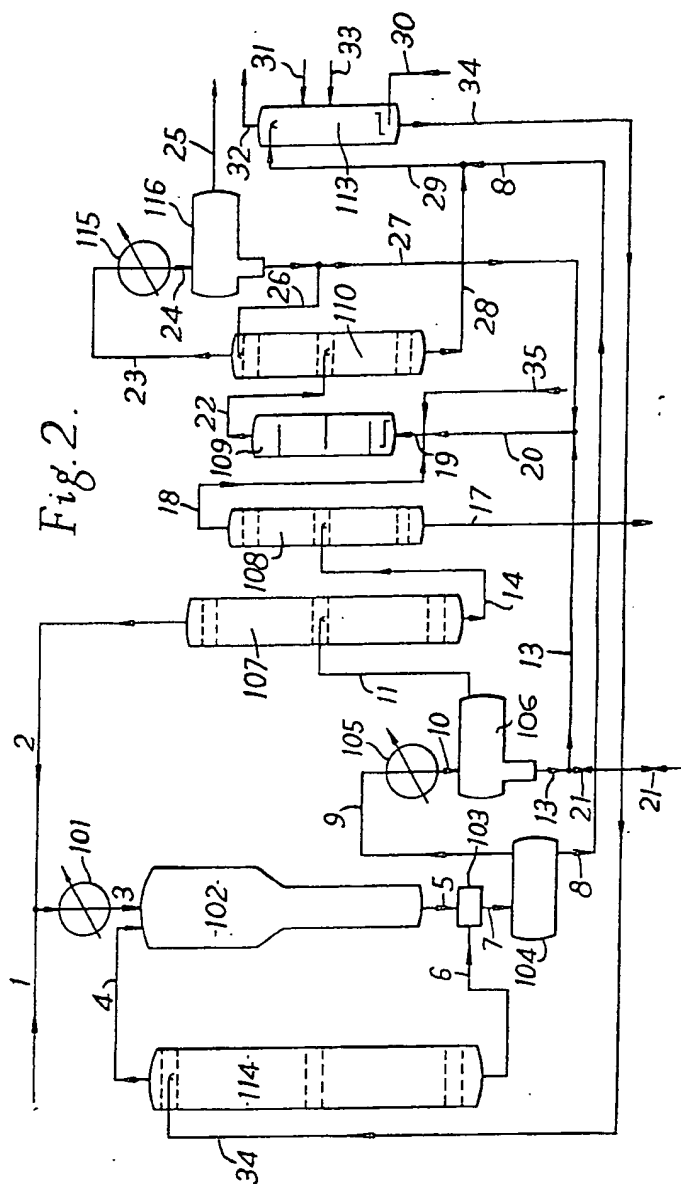
COMPLETE SPECIFICATION

*This drawing is a reproduction of
the Original on a reduced scale
Sheets 1 & 2*

Fig. 2.

Fig. 1.